Studies of the Processes Operative in Solutions. XXIV.—*The Nature of the Hydrolytic Process.*

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(Received July 29,—Read December 5, 1912.)

1. The inquiry described in previous parts of these studies, as well as in the parallel series of studies (I–XVIII)* on the action of enzymes and in that on certain osmotic phenomena (I–IV),† was undertaken primarily with the object of elucidating the nature of the processes operative in solutions, especially of the phenomena of hydrolysis, whether conditioned by ordinary agents or by enzymes, though other important issues have also been dealt with. It now appears to be desirable to consider the general character of the results and to discuss their bearing on current views, so much having been done to throw light on the nature of the changes occurring in solutions.

2. At the outset, we would urge that it cannot be denied that the phenomena presented by solutions are complex in character and that on this ground alone the simple explanation advanced by the advocates of the ionic dissociation hypothesis is highly improbable.

3. It appears to us that many of the conclusions arrived at in the past are to be regarded with the gravest doubt, the assumptions made being of too simple a nature—more especially because the all important part played by the solvent has been often either entirely neglected or insufficiently considered.

The very existence of the solvent has been tacitly ignored by a majority of workers in discussing the properties of solutions, the *volume* of the solution having been considered of greater importance than the proportion of solvent to solute. This has been almost universally the case in discussions of rates of interaction based on the principle of mass action. In too many instances, possible changes in the degree of molecular complexity, both of solute and of solvent, of the latter especially, have been disregarded; moreover, influences have been overlooked which are not commonly recognised as chemical in character, such for example as the large and opposite influence exerted by cane sugar and butyl alcohol on the solubility of salts in water.

4. It may be urged here that the law of mass action, to which appeal is so constantly made, can only be *postulated*—that it is a commonsense generalisation based upon kinetic principles alone, true of an ideally perfect gas but of no other condition. Strictly speaking, the law cannot be *deduced* from the study of solutions, because these cannot afford the required conditions of

* 'Roy. Soc. Proc.,' 1904–12.
† *Ibid.*, 1906–11.

simplicity—and if the results obtained appear to be open to a simple inter-
pretation in accordance with the law of mass, it is because the disturbing
effects counterbalance one another. Such a law *must* hold good in effect—
the difficulty we have is in determining what are the active masses con-
cerned; we can only guess at these, as a rule. Only in very dilute solution
can the active mass of a solute be taken as proportional to its concentration.
In concentrated solutions probably the number of *active units* in a given
volume is never proportional to the assumed number of molecules present, *i.e.*
to the concentration; moreover, alteration of concentration probably changes
the degree of activity of the active units. Other causes also may condition
divergence from constancy in the calculated velocity coefficient. In the case
of the hydrolysis of cane sugar, for instance, in which both sugar and acid
must be supposed to be " hydrated," it is not only in no way certain that the
degree of hydration of the substances finally present is the same as that of
the original substances but it is beyond doubt that as the number of
molecules in solution changes, as the interaction proceeds, the " osmotic "
conditions must vary throughout the process. It can scarcely be supposed
that such changes are without effect on the chemical process and the
apparent constancy not infrequently observed may be due, in great measure,
to the balancing of opposed effects. In fine, it is beyond doubt that far too
little care is used in interpreting the results arrived at by the application of
the law of mass action and that many erroneous conclusions have been drawn.

5. Similar considerations apply to all cases in which physical methods of
studying the changes in solutions are used—for example, to determinations
of molecular weight by the cryoscopic method. Thus, it cannot be asserted
that because two non-electrolytes produce the same depression of the
freezing point of water when dissolved in it in certain proportions, they are
therefore present in solution as molecules of the relative weight corre-
sponding to the proportions used; the more soluble is presumably the more
hydrated and its solution more concentrated therefore than that of the less
hydrated but this latter probably will have more effect in simplifying the
complexes present in water: if the greater concentration produced by
the one just serve to balance the greater effect on the water produced by
the other, the molecular weights may well be in the expected ratio but the
agreement between fact and hypothesis only apparent. We call attention
specially to this case in order to lay emphasis on the importance of taking
into account both the function of the solvent and also of the changes produced
in it; the effect of these latter has been overlooked almost universally.

6. The contention originally advanced by A. Williamson in 1850 involved
only the assumption that salts in solution were in a state of continual flux

and constantly interchanging radicles—an assumption which is entirely in accordance with all subsequent observations on the physical properties of solutions; it in no way involved the conception of dissociation. Williamson was content to call attention to a process at work in solutions but did not attempt to explain its nature; he only pointed out its general character and what must be its effect. To account for the electrical conducting power of solutions, the conception of dissociation into *separate* ions was introduced by Clausius in 1857 but this philosopher attributed the change to kinetic causes alone. Influenced by Williamson and Clausius and especially by Helmholtz, who meanwhile had introduced the conception that the atoms carry the number of unit charges of electricity (Johnstone Stoney's electrons) corresponding with their valency, Arrhenius in 1883 first put forward the view that substances in solution are in many cases all but completely dissociated into electrically charged ions; secondly, that these ions are the active part of the solution: or in other words, that electrical conductivity is to be correlated with chemical activity; and thirdly, that the degree of "electrolytic dissociation" is the more nearly complete the more active the substance and the more dilute the solution. It is well known that the view soon became popular.

7. Arrhenius paid no attention to the solvent and his disciple Ostwald, in particular, asserted that—as Kohlrausch had previously argued—it merely played the part of a screen.* At a later date, when it became necessary to admit that the solvent was not inert, it was assumed that water was specially active as a dissociating agent on account of its high specific inductive capacity.†

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* In the discussion at Leeds in 1890 ('Brit. Assoc. Rep.,' p. 335), Ostwald, after referring to the fact that, at ordinary temperatures, no pure liquid is an electrolyte, remarked : " The theory of Arrhenius is still, on this point, the only one which explains this strange fact ; pure liquids do not conduct because their molecules have no space to resolve themselves into ions. It is, therefore, not improbable that water would conduct electrolytically if we could find a suitable solvent for it." But no such solvent has been found—or ever will be apparently. Hydrogen cyanide—a good solvent of water and a liquid of very high specific inductive capacity—has been shown by Walden to be without effect on water ('Trans. Faraday Soc.,' 1910, vol. 6, p. 71).

† It is far too frequently left out of account that the explanation put forward by J. J. Thomson and Nernst is one which involves merely a loosening of the bonds of attraction between the two ions of the " electrolyte " under the influence of water—not an actual separation of the ions such as is required to account for the increased effect exercised by electrolytes in comparison with non-electrolytes, assuming the kinetic explanation of osmotic pressure put forward by van't Hoff to be correct. It is a noteworthy fact, on which we would here lay stress, that the substances which manifest high specific inductive capacity are all relatively simple compounds of compact structure and therefore such as are most likely to form molecular complexes—it may well be that the high specific inductive capacity they possess is due to this circumstance.

8. We venture to insist on the importance of attention being paid to the views advocated by so high and impartial an authority as the late Prof. FitzGerald in the Helmholtz Memorial Lecture which he delivered to the Chemical Society in 1896. To quote a few passages bearing specifically on our contention :—

"So far as we can deal with solids and liquids as statical systems, we may be quite certain that other than electrical forces *must be* postulated. . . . . we must assume other forces than electrical ones or any others varying inversely as the square of the distance. Take, for instance, the suggestion that when an electrolyte is subject to electrostatic induction the superficial induced charges are due to a layer of electrified ions upon its surfaces. If there were no forces other than electrical ones, these ions would fly off the surface like dust. The pressure of the surrounding gas would certainly not prevent this, for a gas never prevents the diffusion of atoms. Hence we must suppose that there are other than electrical forces keeping these ions attached to the liquid. Helmholtz himself states as a conclusion of his investigation of the action of reversible electro-chemical actions—'A remarkable feature in these processes appears to me to consist in the fact that the attraction of the water to the salt to be dissolved can constitute so great a part of the chemical force acting between the oppositely propelled elements.' There seems to be considerable danger that these forces may be neglected. So much advance has been made by assuming that bodies in solution behave in some respects like the same body in the gaseous state that there has been a serious danger of assuming that the physical conditions are all alike."

"It is, no doubt, a most remarkable thing that osmotic pressure should be even roughly the same as what would be produced by the molecules of the body in solution if in the gaseous state but to imply that the dynamical theory of the two is at all the same or that the dynamical theory of a gas is in any sense an *explanation* of the law of osmotic pressures is not at all in accordance with what is generally meant by the word 'explanation.' These osmotic pressures are much more closely connected with Laplace's internal pressure in a liquid, which is essentially dependent on the forces between the molecules, than with the pressure of a gas, which is essentially almost independent of the forces between the molecules."

"It is almost impossible to explain dynamically the supposition that *free* ions with their electrical charges are meandering about in the liquid in a condition that can be at all rightly called dissociated. The term 'dissociated' should be confined to a condition in which the components of a molecule are not connected by any chemical bonds at all. In that case they can diffuse freely and independently through porous diaphragms. Hence the possibility of this independent diffusion is the simple and necessary test of the independence of the components which can rightly be called dissociation. In an electrolyte there is *not* this independence. . . . Without some other important actions existing at the same time such a condition is dynamically impossible and although to consider the matter from this point of view may help us very much, because it gives us a rough and ready analogy to work on, yet there is great danger that it may stop important advances by an illusive appearance of explanation."

FitzGerald even speaks of the "so-called freedom" of the ions as "due to their being in complete bondage with the solvent." He goes on to say—

"That atoms or molecular groups within a molecule often can and do exchange places is quite in accordance with chemical phenomena. That they should do so of their own accord *when the molecules are arranged in a particular way* is also quite in accord with

such phenomena as crystallisation, where the molecules, of their own accord, arrange themselves into the crystalline form *if* they are first polarised by near approach to the surfaces of a crystal but not otherwise, as is evident from the well-known phenomena of supersaturation. These crystalline forces are able not only to arrange the molecules in the solution but to move massive crystals and it is an important matter for investigation whether they are simply electrical or of the more complex type of chemical action. This is perhaps the simplest example of so-called catalytic actions where change is induced by the presence of a material which itself is unchanged and shows the extensive applicability of the general principle that chemical changes depend upon particular arrangements existing and go on of their own accord so long as the arranging power exists. It is conceded that electrolysis and its consequences can be explained by this hypothesis and the only outstanding phenomenon that does not obviously come under this explanation is that of why osmotic pressure is the same or approximately the same as the gaseous pressure of the same number of molecules and which is supposed to be 'explained' by saying that the molecules in the solution are free. This so-called explanation is, however, as I have already pointed out, not a dynamical explanation at all, it is only a very far-fetched dynamical analogy. Thus this supposed advantage of the free ion theory is not only illusory but misleading."

9. The methods of discussing experimental data advocated by Arrhenius and others are valid not only on the assumption they have made that the substance is dissociated into free ions which alone are active; they are also valid on the more general assumption that a portion of the solute is in some way *activated*. It is important, on this account, that the term *ionisation* should not be used except as an indication that a medium has acquired a conducting state—it should in no way be used as an implication of dissociation into separated free ions; nor should the term *ion* be used otherwise than to indicate the parts or radicles into which a substance is separable by an electric current—the sense in which it was used by Faraday.

10. The hold that the ionic *dissociation* hypothesis has taken upon the imagination of late years is such, however, that almost all workers have applied the conception, particularly those who have sought to explain the phenomena of hydrolysis and etherification.

Even the view has been advanced that not only electrolytes but also non-electrolytes—ethereal salts and the complex sugars, for example—may be regarded as dissociated into ions and that the function of the catalyst in hydrolysis is merely to increase the number of the interacting dissociated ions. The chief advocate of this extreme view, Euler,[*] represented the equilibrium between ethylic acetate, water, ethylic alcohol and acetic acid in the following manner :—

$$[CH_3CO][OC_2H_5]+[H][OH] = [CH_3CO][OH]+[H][OC_2H_5].$$
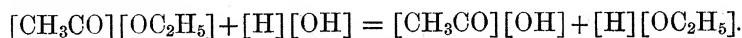
11. The literature of hydrolysis and of the reverse change (etherification)

[*] 'Zeit. phys. Chem.,' 1901, vol. 36, p. 405 ; 'Öfvers. K. Vet. Akad. Stockholm,' 1899, vol. 56, p. 309.
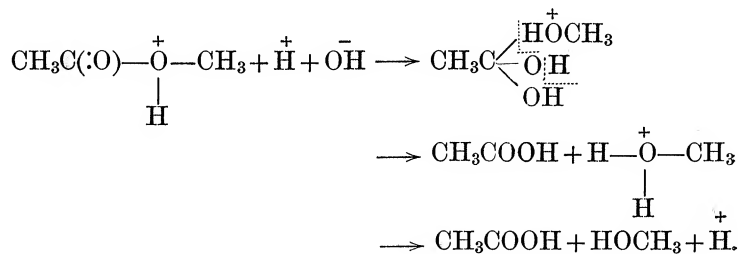
is now overwhelming.   We thought, at one time, that it would be desirable to present a succinct summary of the numerous publications but after spending much time studying them and preparing such a summary, it must be confessed somewhat unprofitably, we have been forced to conclude that it is impossible to do justice to the subject within reasonable limits of space and that the barest reference only can be given to the various hypotheses that have been advanced.

12. The question at issue is one of great importance, as it concerns the whole field of aqueous solutions, including vital phenomena; but it is one of broad principle rather than of detail.   Chemists have to decide whether or no *dissociative* or *associative* changes are at the origin of chemical processes. Hitherto this issue has not been fairly faced.

13. The views of those who postulate the occurrence of ionic dissociation in hydrolysis may be broadly summed up as follows :—(1) In the first stage of the change, a complex positive ion is formed from the acid catalyst and the hydrolyte : in the opinion of some, this is produced by the direct union of the dissociated hydrogen ion of the acid with the hydrolyte ; in that of others, by the combination of the hydrolyte with the two dissociated ions of the acid, the salt so formed being at once resolved into the negative ions of the acid and a complex positive ion containing the hydrogen ion of the acid.   (2) The ultimate products of hydrolysis are formed in a second stage by the action of water on the complex positive ion formed in the first stage—the water acting, some think, in a dissociated form whilst others suppose that the molecule as a whole is active.
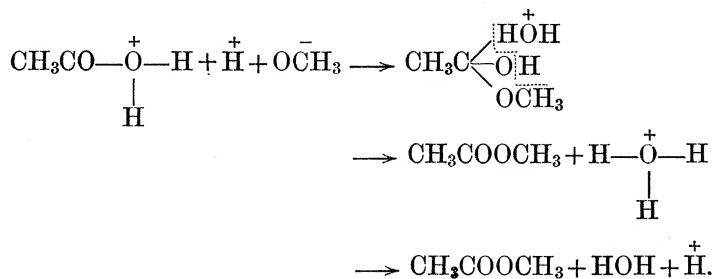
The changes attending etherification are regarded as similar in character to those involved in hydrolysis.

Stieglitz,[*] for example, who is one of the chief workers on the subject, has represented the hydrolysis of methylic acetate in the following manner :—

$$CH_3C(:O)-\overset{+}{O}-CH_3+\overset{+}{H}+\overset{-}{OH} \longrightarrow CH_3C\overset{\overset{+}{HOCH_3}}{\underset{OH}{\diagdown \underset{..}{O}H}}$$
$$\underset{H}{|}$$

$$\longrightarrow CH_3COOH+H-\overset{+}{\underset{\underset{H}{|}}{O}}-CH_3$$

$$\longrightarrow CH_3COOH+HOCH_3+\overset{+}{H}.$$

* 'Amer. Chem. Journ.,' 1908, vol. 39, p. 60.

The formation of the acetate is represented by similar expressions—thus

$$CH_3CO-\overset{+}{O}-H+\overset{+}{H}+O\overset{-}{C}H_3 \longrightarrow CH_3C\underset{OCH_3}{\overset{\overset{+}{HOH}}{<}\ddot{O}H}$$

$$\longrightarrow CH_3COOCH_3+H-\overset{+}{\ddot{O}}-H$$
$$\underset{H}{\big|}$$

$$\longrightarrow CH_3COOCH_3+HOH+\overset{+}{H}.$$

14. The hypotheses referred to all involve the assumption that the rate at which hydrolysis proceeds is proportional to the concentration of the dissociated hydrogen ions present and the numerous supporters of this view are emphatic on the point that this deduction is in agreement with experimental fact.

Thus to quote Stieglitz,* " In the case of the catalysis of the esters we are certain of three main facts which have been proved experimentally: the action is accelerated in proportion to the concentration of the hydrogen ions present; the acid appears to remain unchanged throughout the course of the action, to remain uncombined with any of the compounds involved; and the ultimate condition of equilibrium is not measurably changed by the presence of the acid."

Acree and Johnson,† whose views differ from those of Stieglitz in that they assume that the water acts in an undissociated form, referring to their explanation say, " The assumption explains . . . . . why the velocity of saponification and of esterification increases directly in proportion to the concentration of the hydrogen ions. It further makes clear . . . the experimentally established fact that the equilibrium of the system is not appreciably changed by a change in the concentration of the hydrogen ions. These ideas . . . . have received very good experimental verification."

15. We have no hesitation in asserting that the facts are not in accordance with these assertions.

The upholders of the ionic dissociation hypothesis have been forced to assume that the dissociated " hydrogen ion " is the effective agent in hydrolysis. The contention that the rate of hydrolysis is proportional to the concentration of this ion, however, is based solely on the fact that in the case of a series of acids, their molecular activities, as Ostwald was the first to show, are roughly proportional to their molecular conductivities

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* *Ibid.*, 1908, vol. 39, p. 30.

† *Ibid.*, 1907, vol. 38, p. 341.

and therefore, *ex hypothesi,* to the degree of their ionic dissociation. But those who have discussed the subject appear to have been so led astray by the dissociation hypothesis that they have ignored the well known fact that the rate of hydrolysis increases at a greater rate than the concentration of the acid, instead of at a lower rate, as it should if the rate were proportional to the concentration of the hydrogen ions—in other words, the molecular hydrolytic activity of an acid increases with concentration while the presumed degree of ionic dissociation, deduced from conductivity measurements, decreases. It is remarkable that this fact should be neglected so persistently, as it is *at complete variance* with the explanations based upon the ionic dissociation hypothesis that have been given of the phenomena of hydrolysis.

Ostwald himself appears to have been the first to draw attention to the fact that the rate of hydrolysis of methylic acetate increases more rapidly than the concentration of the acid. Thus, after quoting his results, he remarks :—" Die Geschwindigkeit nimmt also mit steigender Verdünnung etwas schneller ab als die Säuremenge, was wohl aus der Schwächung der Säure durch die zunehmende Wassermenge erklärt werden kann."*

The following year, having been converted meanwhile to the views of Arrhenius, with the express object of contrasting the molecular invertive power of the acid with the molecular conductivity, he extended his observations to the hydrolysis of cane sugar by chlorhydric acid : he again found that the former decreased while the latter increased with dilution. In order to explain the absence of the proportionality which the dissociation hypothesis led him to expect, he assumed that some secondary influence was at work.

Two years before Ostwald's results were made known, Urech had drawn attention to the fact that the rate of inversion of cane sugar increased more rapidly than the concentration of the acid. In a later communication† he again discussed the influence of concentration of the acid, drawing attention at the same time to the fact that Wilhelmy, in his classical investigations published in 1850, had specially pointed out that an increase takes place in the velocity constant which is not proportional to the increase in concentration but greater.

No better illustration could be given of the way in which pioneer work can be overlooked and in which preconceived opinion may operate in precluding discussion of an issue of importance. No explanation has been given of the lack of correspondence between molecular hydrolytic activity and molecular conductivity by the supporters of the ionic dissociation

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* 'Jr. pr. Ch.,' 1883, (2), vol. 28, p. 449.
† 'Ber. deut. chem. Gesell.,' 1884, vol. 17, p. 2165.

hypothesis; the quotations given above are proof that the very existence of the discrepancy has been ignored of late.

16. With regard to the statement made so emphatically by Stieglitz and by Acree and Johnson that the condition of equilibrium attained to in the hydrolysis of ethereal salts is unaffected either by the presence or by the concentration of the catalyst, all that can be said is that the assertion is entirely unsupported by experimental evidence and has probably been made through overconfidence in the explanation.   In Part XXIII it is shown that the percentage of methylic acetate hydrolysed at equilibrium decreases to a marked extent as the concentration of the chlorhydric acid is increased; and Lapworth has obtained similar results, using ethylic acetate.

17. Finally, it may be pointed out that the ionic dissociation hypothesis does not in any way account for the all important fact that the hydrolytic activity of acids is much increased in presence of their salts.

18. The various hypotheses based on dissociation that have been put forward in explanation of the phenomena of hydrolysis and etherification are not only not in harmony with the experimental facts but are also involved and make it necessary to postulate changes which are not only purely hypothetical but also improbable if not impossible; their advocates also do not take into account the action of the solvent water on the various substances, except its supposed power of inducing "ionic dissociation."

In confirmation of our view, we may point to the confusion that has arisen of late among the advocates of the ionic dissociation hypothesis and to the admission that has been made that it is to be supposed that the catalytic activity of acids is a composite effect to be ascribed not only to the dissociated hydrogen ion but also to the undissociated acid.*

We are convinced not only that the processes of hydrolysis *can be* rationally explained without the aid of the ionic dissociation hypothesis but that the chemical activity of acids *cannot* be explained by means of this hypothesis.

19. The explanation that we desire to advocate here is that hydrolysis is an *associative* process initially and that it is effected by the breakdown of a system composed of the hydrolyte, the catalyst and water.   According to our present view, hydrolysis is due to the association and direct inter-action of two complexes—of a single unit of the hydrated hydrolyte with one of the hydrated catalyst.

We imagine that such systems are constantly being produced, broken

* Report of meeting of German Bunsen Society, 'Chemiker Zeitung,' May 25, 1912, p. 587; 'Zeits. Electrochem.,' 1912, vol. 18, p. 539; 'Amer. Chem. Journ.,' 1912, vol. 48, p. 352.

down and re-formed in such manner that, while some give rise to their original components, others are resolved into the products of change; in other words, only a fraction of the unions are effective.

Free water, *i.e.* water uncombined with the hydrolyte or catalyst, does not enter into the interaction.

Hydrolysis, according to this view, is a bimolecular interaction, the second factor being, however, not as is generally supposed, the concentration of the water but that of the hydrated catalyst. The fallacy which underlies the usual interpretation of the mass action equation expressing the condition of equilibrium in the case of the hydrolysis of ethereal salts, in which the proportion of water is one of the factors in the equation, has been pointed out in Part XXIII.

Etherification is to be regarded as a direct reversal of the process of hydrolysis.

20. We would further affirm that the similarity of the results arrived at by the study of the various properties of solutions, such as conductivity, chemical hydrolytic activity and osmotic effects, is due to the fact that the determining factor in all these cases is the interaction involved in the production of the electrolyte from water and the solute.

Increase of molecular conductivity to a maximum on dilution appears to us to be due mainly to two causes—(1) to the gradual increase in the extent of the interaction between the dissolved substance and water; (2) the gradual simplification of the complexes of the dissolved substance.

There is a marked resemblance between the curves showing the increase in the apparent molecular hydration attending dilution (see Diagram 2, Part XXII) and the well-known curves representing the increase of molecular conductivity. In Diagram 1 the two curves in the case of sulphuric acid are superposed and fall sufficiently together to justify the suggestion that molecular conductivity is proportional to the apparent molecular hydration. In the case of chlorhydric acid, the curves do not lie so close together, that representing the apparent hydration rising more rapidly in dilute solutions. It is pointed out in Part XXIII, however, that the somewhat rapid rise in the values of the apparent molecular hydration in the case of this acid in dilute solution may possibly be due to experimental error.

Decrease of molecular chemical activity—of the hydrolytic activity of acids for instance—to a minimum on dilution appears to be the necessary outcome of a gradual weakening of the acid by further combination with water. It is rational to suppose that the more the activity of the acid is used up in combining with water, the less residual activity it will have to
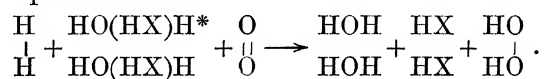
effect hydrolysis, for instance. This is no new idea but one which has long been held by chemists and a necessary consequence of the fact that heat is evolved as solutions are diluted—a circumstance in no way taken into account in the ionic dissociation hypothesis.

It is a great weakness in the Arrhenius hypothesis that it involves the eminently improbable assumption that not only is the change of activity on

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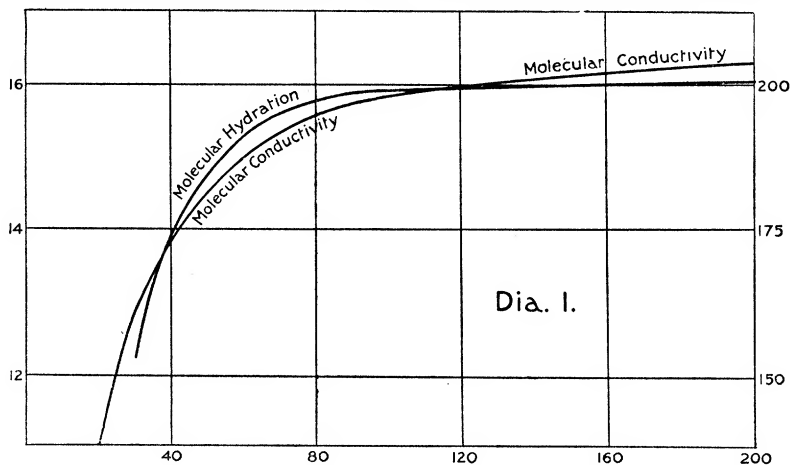
dilution in any particular solution the consequence of an alteration in the mere number of active units but that the activity of the active units of different substances is the same.

21. The body of evidence now available that the process of chemical change is associative, not dissociative, is very great indeed: it is impossible to dispute the conclusion that in order that interaction may take place conditions must prevail such as obtain in a voltaic system. The work of Brereton Baker, for example, in particular, has shown that not water alone but conducting (impure) water—$i.e.$ an electrolyte—must be present to determine change. As the contact difference of potential is equal and opposite at the opposite junctions of two substances, no current can flow in a binary system; to constitute a slope of potential, a third compound must be introduced and one of the three must be an electrolyte. To take an example, there is good reason to suppose that, in all cases, oxidation is primarily a process of hydroxylation effected in a complex circuit such as is pictured in the expression :—

$$\begin{matrix} H \\ | \\ H \end{matrix} + \begin{matrix} HO(HX)H* \\ HO(HX)H \end{matrix} + \begin{matrix} O \\ || \\ O \end{matrix} \longrightarrow \begin{matrix} HOH \\ HOH \end{matrix} + \begin{matrix} HX \\ HX \end{matrix} + \begin{matrix} HO \\ | \\ HO \end{matrix} .$$

* This expression is not used as a representation of the constitution of the electrolyte or of the manner in which it acts but merely as an indication that the electrolyte is necessarily included in the circuit.

22. As the processes of electrolysis and of chemical change, in general, cannot well be regarded otherwise than as reciprocal, inseparable processes, it is to be supposed that electrolysis also is effected in a three component system—in other words, that it is essentially an associative process. In this connexion, attention may once more be directed to FitzGerald's remark in the Helmholtz Memorial Lecture on the importance that is to be attached to "suitable arrangements of molecules"—and to the opinion he expressed that a modified Grotthus' hypothesis will fit the facts.*

The process of hydrolysis differs only from the process of hydroxylation (oxidation) in that the compound hydrolysed is one consisting of two sections, one of which is capable of acting as the positive, the other as the negative element in the voltaic system—capable, therefore, of sharing the two ions of the water molecule between them, the OH radicle being delivered against the positive and the hydrogen radicle against the negative element of the hydrolyte.

23. The selective activity of enzymes and their extraordinary efficiency as hydrolytic agents has been overlooked in common with nearly all the evidence to be derived from the organic side of chemistry; such selective activity is incompatible with the hypothesis that the hydrogen ion is the effective agent in hydrolysis.

But the selective activity of enzymes is not only incompatible with the dissociation hypothesis, it also appears to afford an unanswerable argument in favour of the conclusion that hydrolysis is a process in which hydrolyte and hydrolyst become associated, especially in view of the fact that enzymes which act on glucosides may be specially controlled and their activity diminished by the "glucose" from which the glucosides are derived.
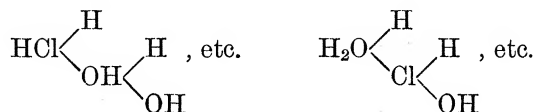
24. The view put forward by one of us in explanation of the activation of "salts" by dissolution in water involves the assumption that solvent and solute are reciprocally active and has the advantage that no distinction is drawn between compounds such as hydrogen chloride (HCl) and hydrone (H_2O), whilst the dissociation hypothesis involves the assumption that they are of an entirely distinct nature and that the one is almost completely dissociated whilst the other is all but unchanged when they are intermixed. It is impossible, on chemical grounds, to admit this latter postulate.

It is assumed that when the two compounds are brought together, whilst the one is "hydrolated" the other is "muriated," thus:

$$HCl + OH_2 = HCl\!\!<^{H}_{OH} \qquad H_2O + HCl = H_2O\!\!<^{H}_{Cl}$$

* 'Brit. Assoc. Rep., Bradford,' 1900, p. 654.

Moreover, that on dilution both of the "associated" compounds become further hydrolated, thus

$$HCl\underset{OH}{\overset{H}{<}}\underset{OH}{\overset{H}{<}} \text{, etc.} \qquad H_2O\underset{Cl}{\overset{H}{<}}\underset{OH}{\overset{H}{<}} \text{, etc.}$$

25. On general grounds and in view of the fact that, on dilution, a point is reached at which the specific electrical conducting power of the mixture is at a maximum, it is probable that in some way or other the two kinds of "associate" are reciprocally active in conveying the current and therefore in all cases of electrolysis (*i.e.* of chemical change, if chemical change always involve electrolysis, as we assume to be the case).

The argument we have in mind in making this statement is not an easy one to appreciate and it will be difficult to determine its validity. We consider that as chlorine and oxygen are in every way analogous elements, their hydrides will tend to behave similarly—whatever is true of the one is true, within limits, of the other. Hence it is to be supposed that when interaction takes place on mixing them, each becomes "distributed" against the other. The new correlated compounds that are formed ($H_2O\overset{H}{\underset{Cl}{<}}$ and $HCl\overset{H}{\underset{OH}{<}}$ and their hydrols) must have similar properties.

One or other of two further assumptions must be made—that, in conveying the electric current, either (*a*) each is active singly or (*b*) they act in conjunction.

Each of the two complexes presumably is less stable than either of the simpler molecules from which they are derived, as the dominant element (chlorine in the one case, oxygen in the other) has a greater burden cast upon it. In other words, H and OH in the complex $HCl\overset{H}{\underset{OH}{<}}$ are less firmly held than they are in hydrone, whilst H and Cl in the complex $H_2O\overset{H}{\underset{Cl}{<}}$ are less firmly held than they are in hydrogen chloride. This view is not only rational but the facts appear to support it.

But the stability of the two hydrides is only lowered by their interaction in the manner pictured—*their ions are not free.* Apparently a lowering of stability is not sufficient to render a compound an electrolyte *per se*—no single substance of simple molecular constitution is an electrolyte. There is much evidence, in fact, to show that, in some way or other, electrolysis is the outcome of an interaction determined by an electromotive force not the consequence of the breakdown of a single substance.

26. To account for the changes that occur when salts are mixed, it is necessary to assume that electrolysis is always taking place within closed circuits in solution and that rearrangements are effected in consequence. When electrodes are introduced, they but tap the circuits and it becomes possible to urge a current along the various chains of molecules normally existent in the solution and to attract the oppositely polarised radicles at the ends of the chains to the oppositely charged electrodes.

It is difficult, in the absence of all positive knowledge on the subject, to give any precise picture of the process. Presumably, the circuit is constituted primarily through the operation of the residual affinity of the negative radicles; once they are constituted, the breakdown involving rearrangement (*i.e.* electrolysis) is immediate in some of the systems, whilst others are merely resolved into their original components. The rate of hydrolysis depends on the proportions in which these two changes take place.

The change may be formulated as follows, using double arrows to indicate the directions in which residual affinity tends to act and dotted lines to show the direction in which cleavage is effected; if read the reverse way the scheme indicates the course of change in etherification :—

Hydrolated
hydrolyte | Hydrolyst
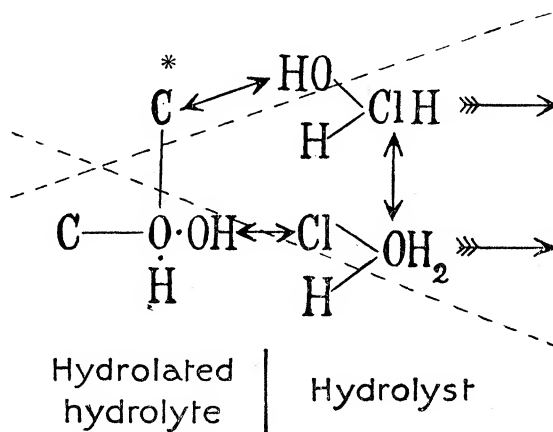
27. The scheme is that applicable to concentrated solutions, in which presumably the hydrolyst is present in its simplest forms; as the concentration is diminished, these give place to more hydrolated and weaker forms, *e.g.*

$$\text{HO-O-O}\ldots\ldots\text{Cl} \quad \text{and} \quad \text{HO-O}\ldots\ldots\text{Cl-OH.}$$
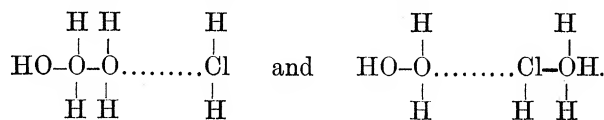
* The oxygen junction of an etheric compound is represented in this scheme.

It is to be supposed that these are immediately active only at one terminal point of each, where presumably the free valencies are situate, so that to represent their action in the diagram it is necessary to lengthen the symbols of the hydrolyst "correlates" only in the direction indicated by the barbed arrows.

If this view be adopted, an interpretation is at hand of the fact on which emphasis is laid in paragraph 20 that molecular hydration and molecular electrical conductivity follow closely the same course, as the solute is shown to be extending its influence as dilution proceeds though it loses strength as an agent.

28. It is to be expected, on the other hand, that acids would be active in the order of their specific electrical conductivity, though molecular conductivity and molecular hydrolytic activity vary on dilution in the case of any one acid in opposite directions, the one diminishing as the other increases. Action within the molecular circuits must follow Ohm's law $(C = E/R)$ but it is not possible to institute any direct or absolute comparison between actual conductivity and hydrolytic activity, owing to the disturbance effected by the hydrolyte and the impossibility of allowing for the amount of free water. In the case of acids, as the concentration is increased, specific conductivity increases to a maximum and then falls. Hydrolytic activity also increases though at a more rapid rate than the concentration, whilst specific conductivity increases at a less rate; but it has not yet been ascertained that it reaches a maximum. Presumably it does but whether the maxima coincide is open to question; it is to be supposed that in the case of hydrolysis complications arise owing to the interaction of the alcohol and the acid catalyst.

29. J. Gibson has argued in a recent communication to the Royal Society of Edinburgh* that the point of maximum conductivity is an all important turning point. He considers that interaction always takes place in such a way as to cause an increase of specific conductivity. Thus an acid catalyst of lower concentration than that corresponding to maximum conductivity, according to Gibson, should favour hydrolysis of ethereal salts, whilst one of higher concentration should favour the reverse change of etherification. Etherification takes place, however, in and is accelerated by very dilute acid solutions, though it does not proceed far: it is probable that hydrolysis also takes place in acid solutions of greater concentration than that corresponding to maximum conductivity.

Gibson's view that acid solutions of maximum conductivity are practically without hydrolytic action on cane sugar does not appear to us to be correct,

* 'Roy. Soc. Edin. Trans.,' 1911, vol. 48, p. 117.

though it seems probable that beyond this concentration of acid the rate of hydrolysis is decreased instead of being increased by further concentration. In our opinion, there is a "tendency towards maximum conductivity" because maximum conductivity is reached when the two constituents of the electrolyte interact in the proportions in which they exercise their maximal reciprocal influence.

It seems to us that actions involving withdrawal of water will take place preferentially on the one side (the acid side) of the maximum and those involving hydrolysis on the other—in other words, it is probable that the point of maximum conductivity is that at which the reciprocal changes are in equilibrium in maximum proportions and that when this point is passed other actions set in. For example, the charring of cane sugar must be an effect produced by the more or less direct interaction of the acid and the cane sugar, as the effect is not observed when dextrose, for example, is acted upon by the acid.

30. According to our view, the process of "ionisation," *i.e.* activation, which gives rise to the hydrolyst is that involved in the interaction of the hydrogen chloride and hydrone, whereby the two "reciprocal" salt forms are produced —but just as no distinction is drawn between the two hydrides and it is assumed that both are activated, so also it is assumed that the hydrolyte is also acted upon in an activated form, namely the hydrol.

The rate of hydrolysis, from this point of view, is dependent on the degree of activation of the hydrolysed substance, as well as on the degree of activity of the hydrolyst.

It is necessary therefore to recognise the existence of strong and weak hydrolytes as well as of strong and weak acids or bases, the strength depending in both cases on the degree of activation through hydrolation (or the reciprocal change).

To make this contention clear, it may be pointed out that hydrolytes generally, from the point of view here put forward, are to be regarded as more or less basic substances in presence of acids. It is assumed that the degree of activation, both of acid (catalyst) and base (hydrolyte), is proportional to the number of molecules in which hydrol is active: ethereal salts, in fact, may be pictured as acting as weak bases more or less comparable with ammonia though weaker.

31. The advocates of the ionic dissociation hypothesis assume that all ions of acids are of equal strength and that the variation in the strength of acids is simply due to variation in the number of ions. This does not appear to be in harmony with general chemical experience—every chemist must feel that sulphuric acid is intrinsically a strong and acetic a weak acid.

According to the view here put forward, the (molecular) strength of an acid depends primarily on its nature ; but presumably it will also vary with concentration, becoming gradually weaker as it is more and more hydrolated.

Weak acids which obey the so-called dilution law are those which are only slowly resolved on dilution into the fundamental molecules and therefore only slowly hydrolated.

The method adopted by the advocates of the ionic hypothesis of determining the degree of dissociation of an acid in a solution (the ratio μ/μ_∞ deduced by taking into account the molecular conductivity at a particular strength and molecular conductivity at infinite dilution) is only valid if the simple assumption be accepted as to the manner in which dissociation takes place on which the advocates of the dissociation hypothesis rely, namely that the whole of the solute is eventually active. If, as argued in previous parts of these studies, " hydration " may take place in various ways and give rise to compounds which are not all active (hydrones as well as hydrols ; compare Part VI, p. 82), the activity of an acid deduced in the manner referred to cannot be regarded as having more than relative value—the proportion of real acid will only reach a certain maximum.

32. In conclusion, we may refer briefly to some of the issues brought under notice in these studies to which special attention may be directed.

33. In the first place, it is claimed that an advance in the method of studying the properties of solutions was made in Part I by referring the concentration of substances in solution to a given mass of solvent (1000 grm. of water, *i.e.* 55·5 molecular proportions) instead of to a given volume of solution, the method previously in vogue. In strong solutions especially, the quantity of dissolved substance in a given volume cannot be altered without greatly reducing the quantity of solvent present, thus introducing a second variable often of considerable magnitude. Throughout the inquiry, volume has been disregarded in making up solutions, the relative molecular proportions of the dissolved substance to a given quantity of solvent being alone considered. The results appear to justify the procedure and to show that the method adopted is that most calculated to bring out the true nature of the effects produced in solutions by alteration of concentration.

The anomalies presented by concentrated solutions made up to a definite volume are either no longer obvious or tend to disappear, the changes produced by alteration of concentration being similar in character throughout the entire range of dilution. The method has been used with like results by Morse and Frazer in their refined studies of osmotic pressure.

34. Though a great improvement, however, the method is not perfect, as

the water which is combined with the dissolved substance in concentrated solutions is often a very considerable fraction of the total water. Consequently, the amount of water *actually free to act as such* must be subject to variation, according as the nature of the substances present is varied and the proportions in which they are dissolved are altered. On this account, it will be very difficult, if not impossible, to unravel all the complexities solutions afford.

35. Throughout these studies, the influence exercised by salts in accelerating hydrolytic changes has been attributed mainly to their concentrating effect— in other words, it is supposed that they enter into combination with more or less of the water present, so that the hydrolytic action of the acid catalyst is effected in a solution the *actual* concentration of which is higher—it may be to a relatively considerable extent—than the *apparent* concentration.

The behaviour of salts, it is well known, is not in harmony with the postulates of the ionic dissociation hypothesis. We submit that the explanation we have advanced is consistent with the facts generally.

36. One main object of the inquiry has been to determine the extent to which salts are hydrated in solutions on the assumption that the increase in the rate at which hydrolysis proceeds is due mainly to the concentrating effect of the salt.

The method first adopted (*cf.* Part I) involved merely the determination of the number of molecular proportions of water that were necessary to reduce the rate of change in presence of a molecular proportion of the salt to that obtaining in the presence of the acid catalyst alone.

Subsequently (*cf.* Part XII), the method was improved in a way which made it possible to deduce apparent molecular hydration values corresponding to different degrees of dilution and it was shown that the values increase with dilution—an entirely rational conclusion. It is realised that though the values referred to are mainly concentration values, they do not necessarily represent the actual degree of hydration of the salts but are rather a measure of the sum of the changes effected in the solution by its presence.

37. A method has been devised (Part XII) whereby also the apparent molecular hydration of the acid catalyst may be determined, at different degrees of dilution, on the assumption that the free water does not enter into the interaction. (The values include the water combined with the hydrolyte, which, however, is very small in amount when only a quarter of a molecular proportion of cane sugar is used to one of acid.)

The apparent hydration values of acids are rather larger than those of the alkali salts and, as in the case of salts, increase with dilution towards

a maximum. The molecular hydrolytic activities of acids, when their concentration is estimated with regard to the free water present, decrease with dilution towards a minimum. This is an important fact, as when their concentration is referred to the total water present it is by no means certain to what extent the increase of molecular activity with concentration is due to the concentrating effect of the acid itself—doubling the proportion of acid to a given quantity of water more than doubling its true concentration referred to free water.

38. It has been shown that when raffinose is used as hydrolyte (Parts XIV and XV) results are obtained very similar to those arrived at with sugar. When, however, methylic acetate is used, the apparent hydration values that are found both of acids and of salts are much lower than when cane sugar is used.

39. The results recorded in these studies show that the apparent hydration values of salts diminish in the case of a series of allied metals as the atomic weight of the metal becomes greater. The apparent hydration values of nitrates are always smaller than those of the corresponding chlorides, bromides and iodides.

It is a well known fact that the general chemical activity of corresponding salts is greater the lower the molecular weight of the salt. The greater activity is to be correlated with the greater concentrating effect of the salt of lower molecular weight.

40. The effect produced by substances other than salts on the hydrolytic activity of acids is in many respects remarkable. Substances such as sugar, which presumably enter into association with a more or less considerable proportion of the water in a solution, *apparently* have little or no influence. It is not improbable that there are compensating influences at work which involve a reduction in the activity of the sugar in a degree corresponding to that in which it is raised by the effect the sugar exercises.

41. The effect produced by alcohols and similar substances having slight affinity for water appears to be quite distinct and different from that exercised by salts and substances such as sugar. This cannot well be ascribed to the withdrawal of water but rather to the mechanical effects produced by interposition of the neutral molecules, affecting both the water itself, the hydrolyte and the hydrolyst.

It is pointed out above that the apparent hydration values, both of acids and of salts, found by means of methylic acetate are much lower than those deduced by using cane sugar as the hydrolyte—this observation is of primary importance, in connexion with the behaviour of non-electrolytes, which have slight affinity for water, to which attention is here drawn.

Methylic acetate is undoubtedly a weak hydrolyte* in comparison with cane sugar and the result arrived at may be the consequence of this weakness, not of any considerable actual lowering of the degree of hydration of either the acid catalyst or the salt.

42. To state in a few brief paragraphs the view which we have been led to form—

Water is a complex mixture of various polymerides of hydrone, OH_2, in equilibrium.

The proportions in which these are in equilibrium is disturbed by the presence of any substance dissolved in the liquid.

"Salts" and other substances exist in solution in combination with hydrone in proportions which vary constantly with the conditions, much water being removed from the sphere of solvent.

The compounds postulated are present in various forms differing in type, only some of the forms being chemically active.

The degree of hydration (hydrolation and hydronation) may vary from the large values characteristic of salts such as calcium chloride to almost *nil.*

We do not believe that salts are ever present in solution in the dissociated condition postulated by Arrhenius. In concentrated solutions, they undoubtedly exist, to some extent, in a polymerised condition; such complex molecules are simplified as dilution proceeds, the simpler molecules become "hydrated" in various ways and to various extents.

The interactions that occur in solution, we imagine, are primarily in all cases associative processes and ultimately the consequence of rearrangements effected within complex molecular systems.

43. We venture to claim that the explanation here given of the process of hydrolytic change is simple, consistent, in harmony with the facts, in accordance with chemical experience and generally applicable. In our opinion, the ionic dissociation hypothesis does not afford an explanation of the facts. We go so far as to assert that there is now sufficient evidence that the hypothesis is a false one.

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* As acids act simply as agents without themselves undergoing change, no difficulty attends the determination of their strength; but the hydrolyte is not simply the reciprocal of the acid, as besides acting in conjunction with the acid it is broken down; the readiness with which change occurs depends therefore not only on the specific activity of the hydrolyte but also on its internal stability.